Ozone-Initiated Chemistry in an Occupied Simulated Aircraft Cabin

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Abstract

We have used multiple analytical methods to characterize the gas-phase products formed when ozone was added to cabin air during simulated 4-hour flights that were conducted in a reconstructed section of a B-767 aircraft containing human occupants. Two separate groups of 16 females were each exposed to four conditions: low air exchange (4.4 h^{-1}), < 2 ppb ozone; low air exchange, 61-64 ppb ozone; high air exchange (8.8 h^{-1}), < 2 ppb ozone; and high air exchange, 73-77 ppb ozone. The addition of ozone to the cabin air increased the levels of identified byproducts from ~ 70 to 130 ppb at the lower air exchange rate and from ~ 30 to 70 ppb at the higher air exchange rate. Most of the increase was attributable to acetone, nonanal, decanal, 4-oxopentanal (4-OPA), 6-methyl-5-hepten-2-one (6-MHO), formic acid and acetic acid, with 0.25 to 0.30 moles of quantified product volatilized per mole of ozone consumed. Several of these compounds reached levels above their reported odor thresholds. Most byproducts were derived from surface reactions with occupants and their clothing, consistent with the inference that occupants were responsible for the removal of > 55% of the ozone in the cabin. The observations made in this study have implications for other indoor settings. Whenever human beings and ozone are simultaneously present, one anticipates production of acetone, nonanal, decanal, 6-MHO, geranyl acetone and 4-OPA.

Brief

Ozone reacted with the surfaces of people and their clothing, seats, carpeting and other materials inside a simulated aircraft cabin to produce a mixture of oxidation products, including saturated and unsaturated aldehydes, ketones and organic acids.

Introduction

In 2006, 750 million passengers boarded commercial planes scheduled in the U.S., flying a total of 8.1×10^{11} miles (*1*). Commercial airliners cruise at altitudes and latitudes at which the ambient ozone level can exceed several hundred ppb (*2*). The aircraft ventilation system supplies pressurized and thermally conditioned ambient air to the cabin. Only a portion of the commercial fleet of airliners is equipped with catalysts that are designed to control ozone in the ventilation supply air (*3*). Consequently, the level of ozone within a commercial aircraft cabin at cruising altitudes may be elevated. Spengler et al. (*4*) reported 80 ppb as the average time-integrated ozone level on 106 flight segments. Spicer et al. (*5*) found average cabin ozone levels at cruise altitude to be between 31 and 106 ppb on 4 flights within the continental United States. When ozone is present in the cabin, it can react with unsaturated organics in the gas phase, as well as with saturated and unsaturated organics on surfaces, to produce volatile byproducts. Hence, passengers and crew are exposed not only to ozone but also to the volatile byproducts of ozone-initiated chemistry.

This paper reports on the volatile byproducts formed when ozone is present in a simulated commercial aircraft cabin containing human subjects, and builds on previous work (*6*) that investigated ozone-initiated reactive chemistry in an unoccupied simulated aircraft cabin. The present experimental investigation, conducted October-November 2005, differs from the previous effort in several respects: it was conducted with human subjects in the aircraft; it utilized multiple analytical methods to identify byproducts; and it used two different air exchange rates to investigate the influence of air exchange on both the chemistry and the levels of the resulting products. The work reported in this paper is part of a larger effort that has also examined the factors affecting ozone removal rates during these experiments (*7*) and the human

subjects' assessment of air quality and self-evaluation of symptoms during the simulated flights (*8*).

Methods

Description of simulated aircraft cabin. Details regarding the simulated aircraft cabin and its operation have been previously reported (*6-9*). In brief, the cabin (width, 4.9 m; length, 3.2 m; cross sectional area, 8.9 m^2; volume, 28.5 m^3) contains three rows of 7 seats each and is installed inside a climate chamber. In the present experiments, outdoor supply air was dehumidified and cooled before passing through a charcoal filter to remove ozone. It then passed through a 10-m^3 mixing chamber before entering the cabin through standard aircraft plenums from two longitudinal slots in the ceiling. On days when ozone was added to the cabin air, it was generated in the mixing chamber. The recirculated air passed through a used HEPA filter but was otherwise untreated. The total supply airflow, including recirculated air, was always ~185 L/s (equivalent to 21 h^{-1}). During the low air-exchange condition, 37.7 L/s was outdoor air (4.4 h^{-1}); during the high air-exchange condition, 75.6 L/s was outdoor air (8.8 h^{-1}). All experiments were conducted at 1 atm pressure. The HEPA filter, supply air plenum, wall panels with windows, seats, and carpet had all seen prior use for extended periods in commercial aircraft. The surface area of the cabin carpet was 15.6 m^2; that of the airplane seats was 24.6 m^2.

Experimental conditions. Ethical review boards in Denmark and the United States approved the use of human subjects for the present experiments. Two separate groups (A and B) of 16 females were each exposed to four conditions: low air exchange (4.4 h^{-1}), < 2 ppb ozone; low air exchange, 61-64 ppb ozone; high air exchange (8.8 h^{-1}), < 2 ppb; and high air exchange, 73-77 ppb ozone. The order in which Groups A and B experienced the four conditions was varied in a

semi-balanced design (Table 1). Each simulated flight lasted 4 hours and took place on Monday, Tuesday, Thursday or Friday of successive weeks. Wednesday of each week was used for background chemical measurements in the unoccupied cabin.

Generation and measurement of ozone. The mixing chamber contained seven UV ozone generators (Jelight Company Inc) that, when in use, were fed with oxygen (99.9999%) from a compressed gas cylinder. On days with ozone in the cabin, the ozone generators were turned on two hours before people entered and adjusted to provide the target ozone level. They were then shut off for one hour and turned back on just after the subjects entered the cabin and the doors were shut. The ozone generation rate was controlled by changing the number of generators that were on and the fraction of each lamp surface that was exposed. Ozone abundances (ppb) in the mixing chamber and simulated cabin were continuously monitored with UV photometric analyzers (Dasibi 1003-AH); sampling points were close to the exhaust of the mixing chamber and behind a seat of the last row in the cabin at a height of 1.2 m

Additional chemical measurements. The CO_2 levels of outdoor and cabin air were monitored at 4-minute intervals using a photoacoustic spectrometer (Brüel & Kjær Multi-Gas Monitor Type 1302). Cabin relative humidity was monitored at 3-minute intervals. Several methods were used to sample and analyze the organic chemicals present in the air of the simulated cabin:

i) Proton transfer reaction-mass spectrometry (PTR-MS) was conducted using full scans that monitored all signals between m/z 20 and m/z 200; this provided continuous measurements of the abundances of volatile organic compounds (VOCs) (*10, 11, 6*). The instrument was calibrated on site using dynamically diluted oxygenate standards (Apel-Riemer Environmental Inc) containing ~1 ppm (accuracy: within ± 5%) of acetone, linear aldehydes up to decanal,

methanol, ethanol, and MEK. A similar response factor was assumed for 6-methyl-5-hepten-2-one (6-MHO) and 4-oxopentanal (4-OPA). For 6-MHO, a 40% fragmentation into m/z=107 ($MH^+ - H_2O$) was taken into account. This ratio was derived from an authentic sample of 6-MHO that was spiked into the cabin air. 4-OPA does not fragment, based on experiments in a small reactor where 6-MHO was ozonized. As previously reported (*12*), the variability of PTR-MS calibration factors was ~ 15-30% for oxygenated compounds such as monofunctional alcohols, aldehydes and ketones. Cabin air was sampled via a Silcosteel™ (Restek Corp) capillary (OD: 1/8", L: 150 cm) at a flow rate of 2.2 STP L min^{-1}. A flow of ~ 30 STP ml min^{-1} was branched off to the inlet of the PTR-MS instrument, which consisted of a pressure-controlled Silcosteel™ capillary (OD: 1/16", L: 15 cm). To determine the instrumental background signals, the cabin airflow was periodically diverted through a mixed Pt/Pd catalyst (Parker Hannifin Corp) capable of removing VOCs with an efficiency >99.9%. No artifacts were observed when the inlet system and the PTR-MS instrument were exposed to VOC-free air containing 50-100 ppb ozone. Additionally, the following cabin conditions, absent occupants, were investigated: 1) elevated ozone, 2) elevated humidity, 3) elevated ozone and humidity. These measurements indicated that no significant by-products were formed in the mixing chamber and that background levels made only small contributions to the VOCs reported in the present study.

ii) Multisorbent tubes containing Tenax-TA® backed by Carbosieve® were used to collect VOCs and were later thermally desorbed and analyzed by gas chromatography with mass selective detection (TD-GC/MS, Agilent 6890/5973) (*13*). Samples were collected in duplicate with a subset analyzed to assess analytical precision. Samples were collected without ozone scrubbers. This introduced a negative bias for compounds with unsaturated carbon bonds (*14-16*), and TD-GC/MS results for such compounds are lower limits. Positive artifacts (*17*) are not anticipated to be large at the ozone levels used in the present study. This inference was validated

by comparing a subset of results from sorption-tube sampling with matching results obtained using PTR-MS.

iii) DNPH-coated silica cartridges (P/N 047205, Waters Corp) were used to sample saturated aldehydes and ketones; an O_3 scrubber preceded each cartridge (WAT054420, Waters Corp.). Cartridges were extracted with 2 mL acetonitrile. Extracts were analyzed for formaldehyde, acetaldehyde and acetone by HPLC with UV detection at 360 nm (Agilent 1200) (*13*).

iv) DNSH-coated cartridges were used to sample unsaturated carbonyls. The collection procedures were analogous to those used for the DNPH cartridges. The samples were subsequently extracted and analyzed using HPLC (*18*). Derivatives were quantified to determine acrolein levels.

v) NaOH-coated silica cartridges (P/N 226-55, SKC West Corp) were used to sample organic acids. These were extracted with deionized water, and the extracts were analyzed by ion chromatography (Dionex Corp) for formic and acetic acids (*19*).

Sampling began one hour after the subjects had entered the cabin; the 1st sampling period was 14:00-16:00; the 2nd, 16:00-17:00. The data reported in the present paper are from the 1st sampling period. The integrated samplers were analyzed at either Lawrence Berkeley National Laboratory (ii, iii, v) or UMDNJ/Rutgers University (iv). Based on duplicate samples and previous experience, the experimental precision was estimated to be 2-20% for carbonyls and 15-70% for carboxylic acids.

Results and Discussion

On days with simulated flights, the passengers boarded and doors closed at 13:00. By 14:00 the levels of water vapor, CO_2 and O_3 within the cabin had reached steady levels. Table 1 reports average values for these parameters for each of the four simulated flight conditions

during the period 14:00-16:00. As expected, flights with low air-exchange rates had higher average CO_2 and RH levels than those with high air-exchange rates (2150 vs. 1285 ppm CO_2; 20 vs. 10% RH).

Table 1. Summary of the average ozone level, carbon dioxide level and relative humidity (RH) measured from 14:00 to 16:00 for each of the eight experiments.

Experiment, Date (2005)	**Group**	**Outdoor air exchange rate** (h^{-1})	**Cabin O_3** (ppb)	**Cabin CO_2**[a] (ppb)	**Cabin RH** (%)
1, Oct 24	A	8.8	73	1285	10
2, Oct 25	B	4.4	64	2255	20
3, Oct 27	A	4.4	< 2	2110	20
4, Oct 28	B	8.8	< 2	1280	10
5, Oct 31	A	8.8	< 2	1280	10
6, Nov 1	B	4.4	< 2	2165	20
7, Nov 3	A	4.4	61	2080	20
8, Nov 4	B	8.8	77	1300	10

[a] The level of CO_2 in outdoor air averaged 430 – 450 ppm during experiments.

For the conditions in which ozone was present in the cabin, its steady-state level averaged 60-65 ppb for the low air-exchange rate flights and 70-75 ppb for the high air-exchange rate flights. Ozone levels in the cabin were much lower when people were present than when they were not — by ~ 70 ppb at the low air-exchange rate and by ~ 50 ppb at the high air-exchange rate. Factors affecting ozone removal rates are explored in a related paper (*7*); reactions of ozone on people and their clothing accounted for more than 50% of ozone's decomposition within the cabin, while aircraft seats accounted for approximately 25%; carpet and other interior surfaces, 10%; and the soiled HEPA filter, 7%.

Sum of detected compounds for the different conditions. For Groups A and B, for each of the four conditions, Figure 1 displays the total, average level (ppb) of gas-phase organic compounds in the cabin air as determined from PTR-MS measurements during the period 14:00-16:00. Also displayed are the time-averaged sum of the acids, aldehydes and ketones and the sum of the alcohols and hydrocarbons; in each case the summation includes only those compounds that have been positively identified with the analytical methods employed in this study. As pointed out in the Supporting Information, the absolute values of the total PTR-MS signal should be regarded as approximate. It is reassuring that the relative changes in total PTR-MS signal are consistent with those displayed by the sum of the quantified compounds.

For otherwise identical conditions, doubling the air-exchange rate halved the levels of measured organic compounds in the cabin air. This finding indicates that these pollutants predominantly originate within the cabin environment and are generated at approximately constant rates for a given ozone condition.

Ozone had a large effect on pollutant abundances within the cabin. For otherwise identical conditions, the total abundance of identified acids, aldehydes and ketones more than doubled when ozone was present in the cabin air. The formation of such compounds is expected owing to ozone-initiated oxidation processes within the cabin. Ozone had less of an effect on the levels of the identified alcohols and hydrocarbons.

The majority of the oxidation products detected in the cabin air were a consequence of ozone's reaction with surfaces rather than gas-phase reactions (see Supporting Information for elaboration).

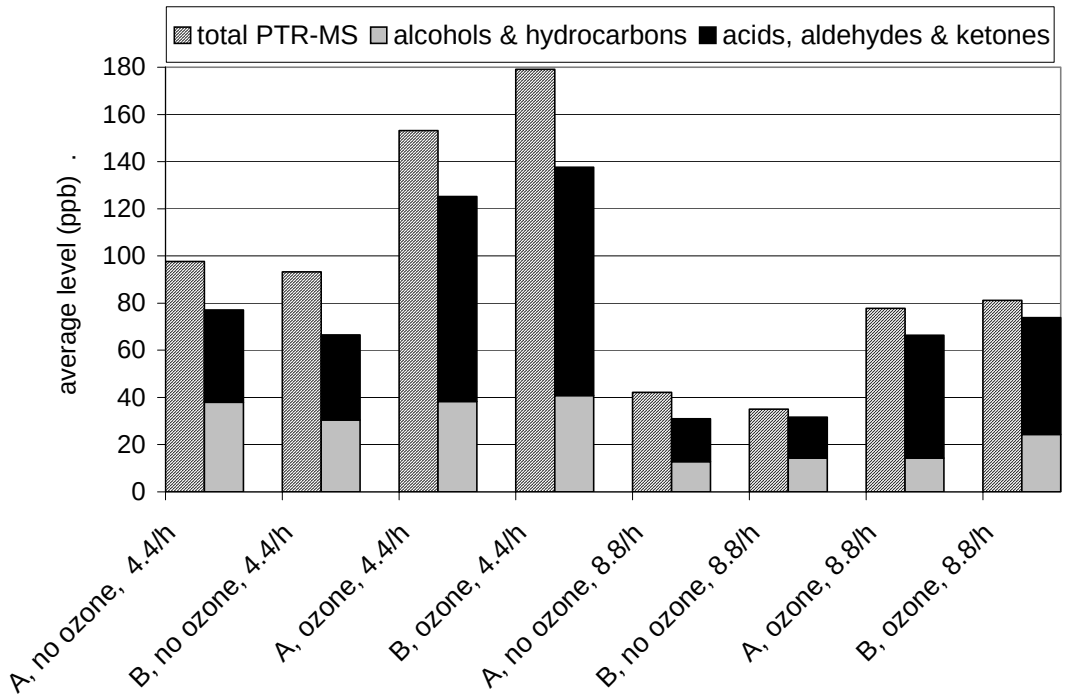

Figure 1. Total levels, determined by PTR-MS, of the gaseous organic compounds in the cabin air during 14:00-16:00 for each of the 8 experiments with human subjects present. Also displayed, as stacked bars, are the sums of the positively identified "aldehydes, ketones & organic acids" and "alcohols & hydrocarbons".

More detailed comparisons among the conditions. Figure 2 shows the cabin air levels of formaldehyde and acetaldehyde (determined by the DNPH method), summed C4-C8 aliphatic aldehydes (multisorbent method) and nonanal and decanal (PTR-MS method) for each of the experimental conditions. The addition of O_3 to the cabin air resulted in large increases in the abundances of saturated aldehydes with 4 to10 carbon atoms. When ozone was present, saturated aldehydes were major contributors to the total abundance of volatile organic compounds measured within the simulated aircraft cabin. The increase was particularly striking for nonanal and decanal; levels without ozone were < 0.80 ppb while levels with ozone were 3 to 8.5 ppb, well in excess of their reported odor thresholds (2.2 and 0.9 ppb, respectively (*20, 21*)).

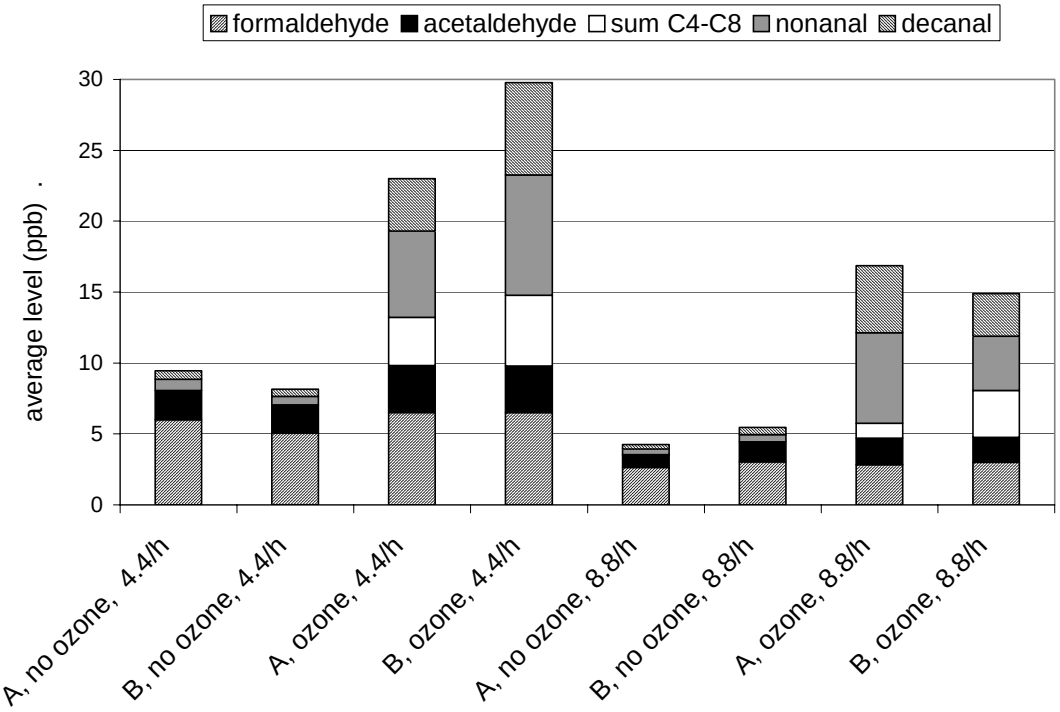

Figure 2. Average levels measured during 14:00-16:00 for saturated aliphatic aldehydes in the cabin air for each of the 8 experiments with human subjects present.

Figure 3 shows the levels of the most abundant unsaturated aldehydes: acrolein (DNSH method), trans-2-heptenal and trans-2-octenal (multisorbent method) and the sum of the nonenal isomers (PTR-MS method). The concentrations of trans-2-heptenal, trans-2-octenal, and the nonenal isomers increased significantly when O_3 was present, although their resultant levels were roughly an order of magnitude lower than those of their saturated analogs. The odor thresholds for selected nonenal isomers are quite low (e.g., 0.15 ppb for trans-2-nonenal (*20, 21*)).

In contrast to the C7 to C9 unsaturated aldehydes, acrolein did not display a clear trend with ozone's presence. Acrolein is a prominent constituent of environmental tobacco smoke (*22*) and is present in the breath of smokers (*23*); it is also generated endogenously under oxidative

stress (*24*). Hence, ozone-initiated surface chemistry is not expected to be the sole significant source of acrolein within the simulated aircraft cabin.

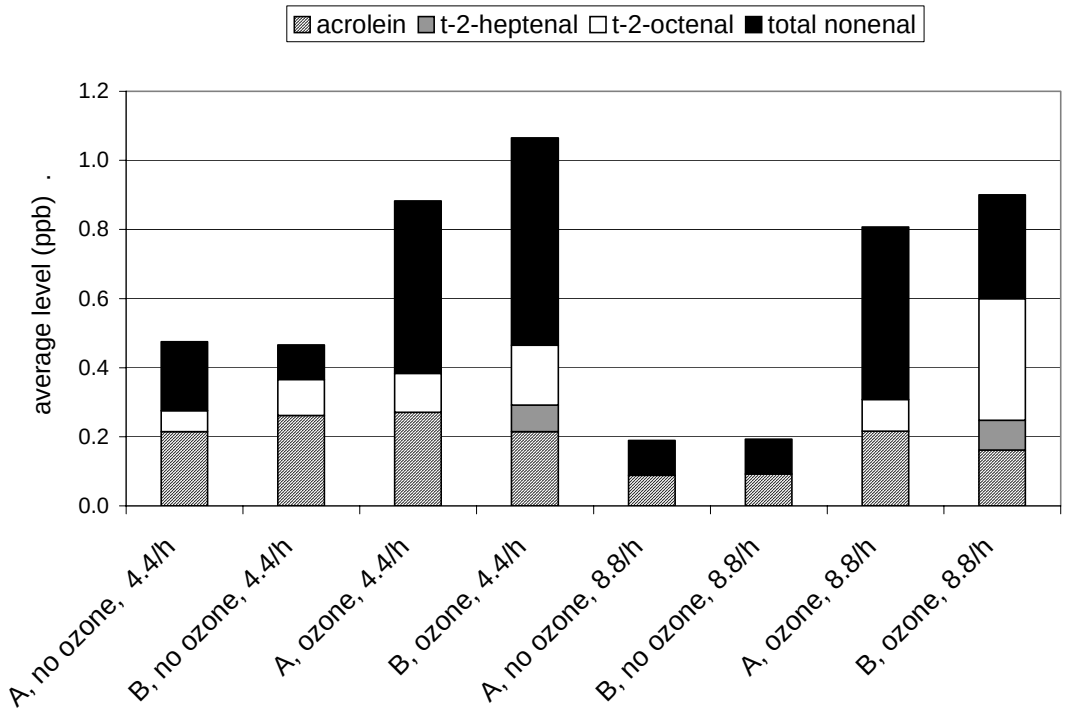

Figure 3. Average levels measured during 14:00-16:00 for unsaturated aliphatic aldehydes for each of the 8 experiments with human subjects present.

Figure S1 in the Supporting Information shows average cabin levels of formic acid (NaOH method) and acetic acid (PTR-MS method) measured during the period from 14:00-16:00. In the absence of ozone, the concentration of acetic acid was several times that of formic. Levels of each increased when ozone was introduced, with acetic acid reaching ~ 10 ppb when the air-exchange rate was low. This level is higher than was observed in the earlier ozone/T-shirt experiments (*6*), suggesting that ozone reactions with the human occupants or their clothing are responsible for a fraction of the observed increase.

Figure 4 shows the levels of acetone, 6-methyl-5-heptene-2-one (6-MHO) and 4-oxopentanal (4-OPA) as determined by PTR-MS measurements. Acetone results obtained by the DNPH method were in excellent agreement with the PTR-MS results. Each of the compounds in Figure 4 is a product of the reaction between squalene, a major component of skin oil, and ozone (*25, 6*). The abundance of acetone, also substantially present in cabin air when ozone was absent, increased by approximately a factor of two when ozone was introduced. The levels of 6-MHO and 4-OPA were below 0.2 ppb in the absence of ozone, but each increased to approximately 3-6 ppb when ozone was introduced. Although not quantified, geranyl acetone, another squalene oxidation product, was also present in the absence of ozone and increased when ozone was added to the cabin air (as indicated by PTR-MS measurements). Comparing Figure 4 to Figure 1, it is apparent that squalene oxidation products were responsible for a significant fraction of the overall increase in "acids, aldehydes & ketones" when ozone was added to the cabin.

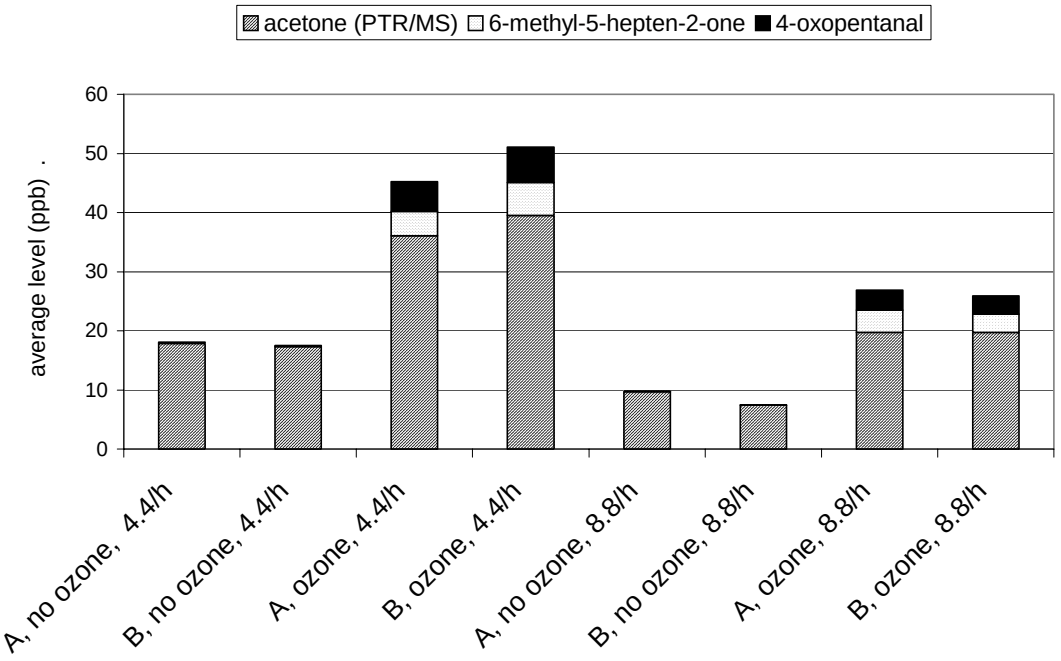

Figure 4. Average levels measured during 14:00-16:00 for squalene oxidation products in the

cabin air for each of the 8 experiments with human subjects present.

Time evolution of oxidation products. The values reported in the previous sections were average abundances measured during the period 14:00-16:00. Figure 5, based on PTR-MS measurements, presents the evolving levels of 6-MHO, 4-OPA and decanal from the time when people first entered the cabin until the simulated flights end. There are separate plots for Group B at 4.4 h^{-1} and Group A at 8.8 h^{-1}. A trace for CO_2 is included in each plot to indicate the time required for an inert constituent of human breath to reach steady levels for these ventilation conditions. The level of 6-MHO reaches a steady value in about 90 minutes at 4.4 h^{-1} and in about 45 minutes at 8.8 h^{-1}. In contrast, the abundances of 4-OPA, nonanal (not shown) and decanal continue to increase throughout the 4-h exposure period at both low and high ventilation rates. The continued growth of 4-OPA may reflect its secondary production from ozonolysis of 6-MHO, while that of nonanal and decanal may be due to the tendency of these higher molecular weight carbonyls to sorb to interior surfaces.

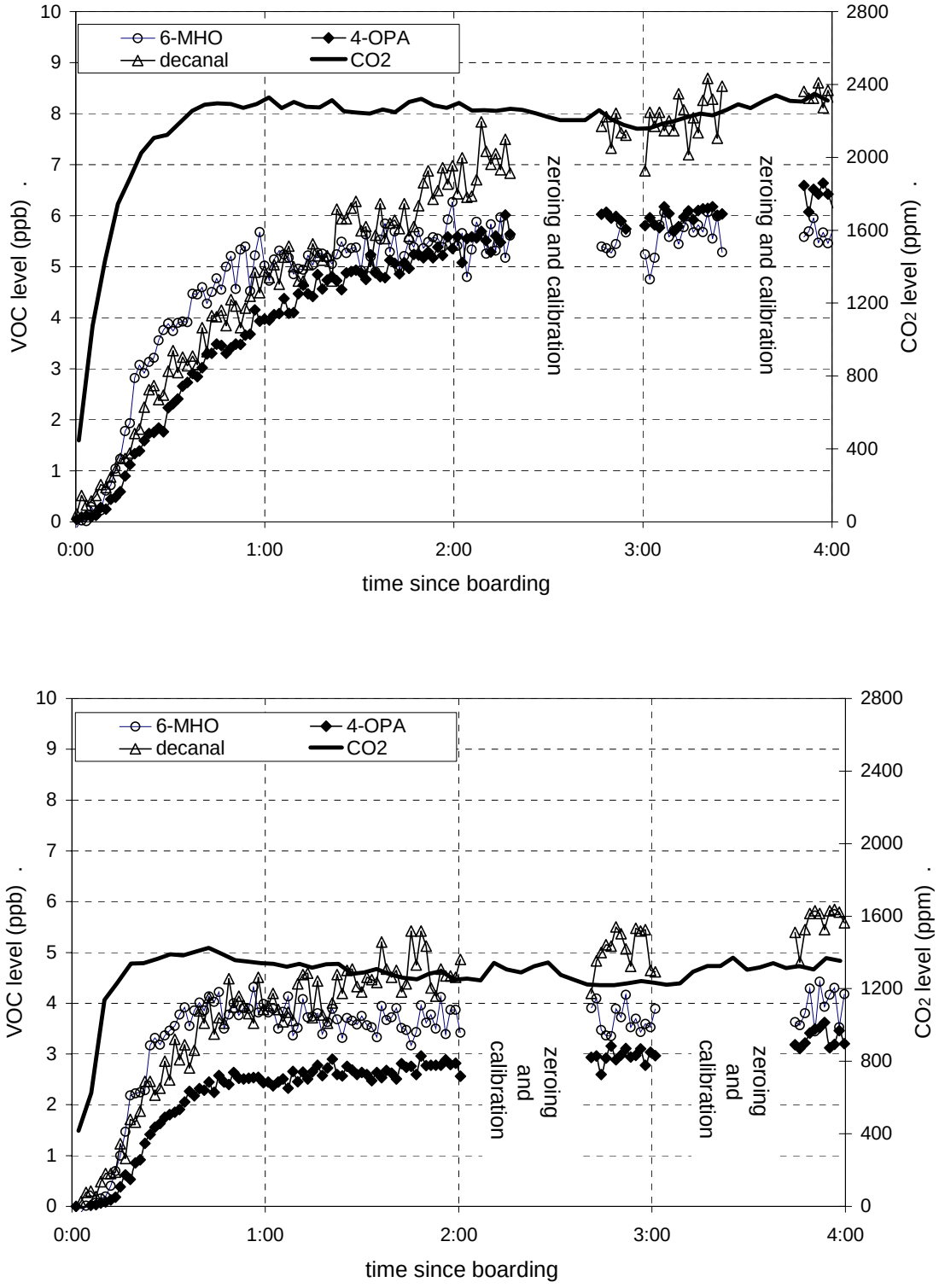

Figure 5. Time evolution of the levels of CO_2, 6-MHO, 4-OPA and decanal for Group B at 4.4 h^{-1} (top frame) and Group A at 8.8 h^{-1} (bottom frame). Data for 6-MHO, 4-OPA and decanal are from PTR-MS measurements.

Yields. Figure 6 shows the yields, defined as the moles of analyte produced per mole of ozone consumed, for the major oxidation products measured in the cabin air. Yields for the identified oxidation products were calculated using a mass-balance model to compare the change in the abundances of the products with the change in the ozone level owing to surface removal. The yields are generally consistent for the four conditions. The major compounds produced when ozone was introduced are acetone, nonanal, decanal, 4-OPA, 6-MHO, formic acid and acetic acid. The overall yield for the identified products was between 25 and 30%. Although the most abundant oxidation products were identified, some less abundant products remain unidentified. When the unidentified oxidation products are included, we estimate that the overall molar yields were ~ 35%, based on the PTR-MS data.

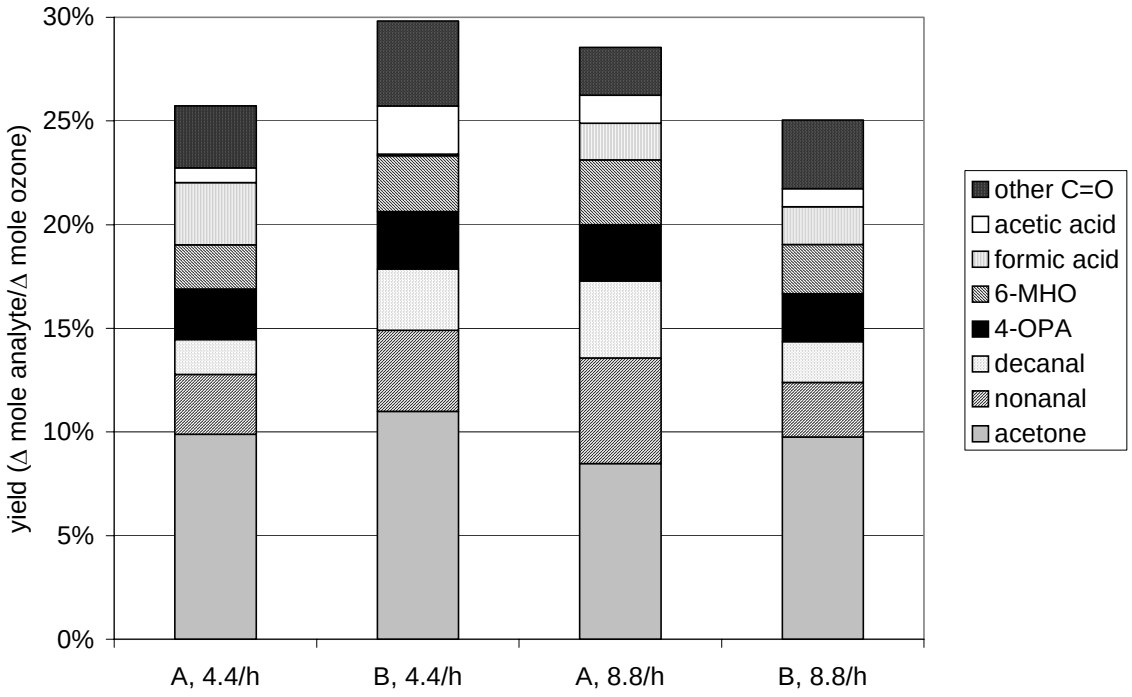

Figure 6. Yields for the major ozone-derived products identified in the cabin air. The uncertainty in the summed yields of the identified products is estimated to be between 15 and 25%.

The yields for the aldehydes measured in this study are in the range of reported yields for aldehydes when ozone reacts with different types of carpets (26) or with various surfaces in homes (27). The overall yields can be most directly compared with those measured in a prior study in this same simulated aircraft cabin (*6*). For ozone reacting with surfaces in the unoccupied cabin, the reported yield was 18%. The yield increased to 24% when 17 previously slept-in T-shirts were placed in the cabin. The presence of people in the current study somewhat increased the yield of oxidation products. Overall, the results of this body of research indicate that surfaces associated with humans are not only important sinks for ozone scavenging in the cabin environment but also important sources for volatile byproduct formation. Skin oils are implicated as major precursors for the ozone oxidation products identified in cabin air (*25*).

Acetone emission rates. Acetone is emitted by various materials; it is present in human breath as a consequence of routine metabolic processes (*28*); and it is produced via the oxidation of numerous precursors, including squalene (*25*). Without ozone or people, acetone levels in the simulated cabin were small: 0.8 ppb at 4.4 h^{-1} and 0.2 ppb at 8.8 h^{-1}. When people were present, but not ozone, the acetone levels reflected basal metabolic activity under sedentary conditions. With 16 people in the cabin, the acetone levels indicated an average acetone emission rate of 0.35 mg/h per person. When people plus ozone were present in the cabin, acetone levels reflected emissions from basal metabolic processes, ozone/occupant reactions, and ozone/cabin surface reactions. Measurements in this study indicate that ozone/occupant reactions contributed 0.39 mg/h per person, comparable to the basal emission rate. (These values were corrected for ozone/cabin surface reactions that contributed 3.0 ppb of acetone at 4.4 h^{-1} and 1.5 ppb of acetone at 8.8 h^{-1}.) The acetone emission rate from ozone/occupant reactions averaged ~ 5.5 μg/h per person per ppb of residual cabin O_3.

Implications of the results. The people in this simulated aircraft cabin, specifically the surfaces of their skin and clothing, were a major sink for ozone (*7*). Acetone, nonanal, decanal, 6-MHO, geranyl acetone and 4-OPA are all produced as a consequence of ozone reacting with human skin oils. The products of ozone interactions with humans account for more than half of the oxidation products identified in the cabin air. These results substantiate the conjecture of an earlier paper (*6*) that occupant density is an important factor to consider when evaluating ozone levels and the extent of ozone-initiated chemistry in commercial aircraft.

The subjects in this study completed questionnaires that provided subjective assessments of air quality and personal symptoms. Detailed results from this part of the study are reported elsewhere (*8*). In brief, of twenty-nine assessments, the subjects judged the air quality and twelve symptoms (including eye and nasal irritation, lip and skin dryness, headache, dizziness, mental tension and claustrophobia) to be significantly worse ($P<0.05$) when ozone was present in the cabin compared to when it was not. The implication is that the presence of ozone and the byproducts of its chemistry contributed to an erosion in the level of occupant satisfaction with cabin air quality and their own sense of well-being.

The observations made in this study have implications beyond aircraft cabin environments. Humans constitute an important site for ozone-initiated chemistry, primarily via reactions with their exposed skin and hair as well as their clothing. Whenever human beings and ozone are simultaneously present, one can anticipate production of acetone, nonanal, decanal, 6-MHO, geranyl acetone and 4-OPA. Because such production is occurring in the immediate vicinity of people, human inhalation and dermal exposures to these byproducts will result. Whether this chemistry plays a role in ozone-associated morbidity and mortality is not known. Such an understanding could influence actions to promote public health, since outdoor-to-indoor

transport of ozone, which markedly influences the degree of exposure to the byproducts of ozone-initiated chemistry, is amendable to modification in aircraft cabins and in other indoor environments.

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Supporting Information Available

An explanation of how the total levels reported in Figure 1 were derived from PTR-MS measurements, Figure S1 showing the average levels of formic and acetic acids for each of the 8 experiments, a discussion of the relative contributions of gas phase and surface chemistry to the products measured in the cabin air, and a discussion of two methods that were used to calculate the yields are available free of charge via the Internet at http://pubs.acs.org.

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